UNIVERSITI PUTRA MALAYSIA

FLAVOUR CHARACYERISATION AND STABILISATION OF FRESH, SPRAY-DRIED AND ENCAPSULATED DURIAN EXTRACT

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By

CHIN SUNG TONG

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirement for the Degree of Master of Science

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Chairman: **Nazimah Sheikh Abdul Hamid, PhD**

Faculty: **Food Science and Technology**

This study concerned the characterisation and stability of flavour volatiles from fresh, spray-dried, freeze-dried and encapsulated durian powder. In the first part of this study, headspace solid phase microextraction (SPME) coupled to fast gas chromatography-mass spectrometry (GC-MS) was applied to analyze the volatile compounds of durian varieties D2, D24, and D101 from Malaysia. Sampling sensitivity was improved by evaluation of sample matrix, sampling size, headspace volume, salt addition and sampling duration. A total of 39 volatile compounds were identified in fresh durian pulp comprising 22 esters, 9 sulfur-containing alkanes, 3 thioacetals, 2 thioesters, 2 thiolanes, and 1 alcohol. The relative amount of volatiles estimated using 1ppm internal standard, revealed differences in the volatile composition among varieties. Further classification and characterisation of each durian variety was successfully conducted using Principal Component Analysis (PCA) whereby PC1, which explained 35.36% of variance, distinguished variety *D2* from *D24* while PC2 with 22.10% variance explained, separated the cluster of variety *D101* from *D24*.

Consequently, quantification of the major flavour volatiles in durian (*Durio zibethinus*) that included propanethiol, ethyl propanoate, propyl propanoate, ethyl 2-methylbutanoate (E2MB) and diethyl disulfide, from fresh, freeze-dried and spray-dried durian pulp as well as effect of drying on the volatiles composition of durian pulp was evaluated using SPME coupled to fast chromatography-time-of-flight-mass spectrometry (fast GC-TOFMS). The correlation coefficients for target volatiles were improved (over 0.97) when surrogate internal standard was used with precision that ranged between 2 and 14%. Overall, spray-drying process, which employed high temperature, induced the formation of several volatiles that included aldehyde, ketone, furan and pyrrole. The loss of flavour volatiles in freeze-dried and spray-dried pulp ranged from 71 to 97% and 97 to 99% respectively.

Finally, changes in durian volatile composition and stability of the major volatile compounds (propanethiol, ethyl propanoate, E2MB and diethyl disulfide) in the spray dry microencapsulated durian powder using 3 types of coating matrices (maltodextrin, gum arabic and lipophilic starch) were evaluated. The flavour release characteristic from the microcapsules stored under different relative humidity, RH (44%, 75% and 92%) at 50°C was further studied. Stability of the microcapsule produced was maintained throughout 20 days of storage without liberation of any volatile acid. Formation of volatiles that included 2- and 3-methylbutanal, 1-ethyl-1-H-pyrrole compounds were induced during the process. Microcapsules prepared from a blend of maltodextrin and gum arabic at ratio 3:1 showed higher volatiles retention. Low volatiles retention in N-Lok microcapsule was observed which probably caused by the

cracking on the surface of its microcapsule. Furthermore, volatiles were released from MG microcapsule at the rate according to Avrami's equation which increased with higher relative humidity in the storage atmosphere.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

PENCIRIAN DAN PENSTABILAN PERISA EKSTRAK DURIAN YANG SEGAR, DIPROSES SECARA PENGERINGAN SEMBUR, PENGERINGAN SEJUKBEKU SERTA PENGKAPSULAN

Oleh

CHIN SUNG TONG

Mei 2006

Pengerusi: **Nazimah Sheikh Abdul Hamid, PhD**

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Kajian ini adalah mengenai pencirian dan kestabilan perisa durian yang segar, diproses secara pengeringan sembur, pengeringan sejukbeku serta pengkapsulan. Dalam bahagian pertama kajian ini, pengesktrakan mikro fasa pepejal pada ruangan tutupan (headspace SPME) bergabung dengan kromotografi gas laju-spectrometri jisim (fast GC-MS) telah digunakan untuk menganalisiskan sebatian meruap dari durian Malaysia jenis *D2*, *D24* dan *D101*. Kepekaan persampelan telah ditingkatkan melalui penilaian bentuk sampel, saiz persampelan, isipadu ruangan tutupan, penambahan garam serta masa persampelan. Sejumlah 39 sebatian meruap telah dikenalpastikan, yang mana terdiri daripada 22 ester, 9 alkana bersulfur, 3 thioacetal, 3 thioester, 2 thilane dan 1 alkohol. Jumlah bandingan bagi bahan ruapan yang ditaksirkan melalui 1 ppm sebatian piawai dalaman, mendedahkan perbezaan komposisi bahan ruapan antara jenis-jenis durian. Pengelasan and pencirian selanjutnya bagi setiap jenis durian telah berjaya dilakukan dangan analisis komponen terutama (PCA) di mana PC 1, yang menjelaskan

35.36% sisihan, membezakan jenis *D2* daripada *D24* manakala PC2 dengan 22.10% sisihan penjelasan memisahkan golongan bagi jenis *D101* daripada *D24*.

Selanjutnya, penaksiran bagi bahan ruapan perisa yang penting dalam durian termasuk propanethiol, etil propanoik, propil propanoik, etil 2-metilbutanaoik (E2MB) dan dietil disulfur dari isi durian yang segar, disembur-keringkan dan disejukbeku-keringkan serta kesan pengeringan ke atas komposis bahan ruapan dari isi durian telah dinilai melalui pengesktrakan fasa pepejal secara mikro (SPME) bersambung dengan kromotografi gas laju-spectrometri jisim masa penerbangan (fast GC-TOFMS). Pekali hubung kait bagi bahan analisis sasaran telah ditingkatkan (melebihi 0.97) apabila sebatian piawai dalaman timbalan digunakan yang mana ketepatan antara sisihan piawai bandingan (RSD) 2% ke 14%. Secara keseluruhan, proses pengeringan sembur, yang menggunakan suhu tinggi, telah merangsangkan penghasilan beberapa bahan ruapan termasuk aldehyde, ketone, furan dan pyrrole. Kehilangan bahan ruapan perisa dalam isi durian yang disembur-keringkan dan disejukbeku-keringkan adalah antara 71 hingga 97% serta 97 ke 99% masing-masing.

Akhirnya, perubahan dalam komposis bahan meruap perisa durian dan kestabilan bahan meruap pentingnya (propanethiol, etil propanoate, E2MB dan dietil disulfide) terhadap prngkapsulan secara mikro melalui pengeringan sembur dengan 3 jenis bahan lapisan pelindung telah dikajikan. Cirir-ciri pembebasan perisa daripada kapsul mikro yang disimpan di bawah kelembapan relatif berlainan, RH (43%, 74% dan 85%) pada 50°C telah dikaji selanjutnya. Kestabilan kapsul mikro terkekal sepanjang 20 hari tersimpan

tanpa kelepasan asid meruap. Pembentukan bahan ruapan termasuk 2- dan 3-methylbutanal, 1-ethyl-1H-pyrrole telah dirangsangkan dalam prosess ini. Kapsul micro yang disediakan daripada campuran maltodextrin dan gum arabic pada nisbah 3:1 (MG) menunjukkan penahanan bahan ruapan yang lebih baik. Bahan ruapan perisa termasuk propanethiol dan E2MB ditahan lebih baik oleh campuran bahan lapisan lindung arabik gum (GA) dan maltodekstrin DE15 (MD) dengan nisbah 1:3. Kecekapan pengkapsulan N-Lok yang rendah telah diperhati yang mana dijangka terpunca daripada keretakan atas permukaan kapsul mikronya. Tambahan pula, nahan meruap terbebas daripada kapsul micro MG pada kadar mengikuti persamaan Avrami yang mana ianya meningkat bersama dengan penambahan kelembapan relatif dalam atmosfera penyimpanannya.

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I certify that an Examination Committee has met on 29 May 2006 to conduct the final examination of Chin Sung Tong on his Master of Science thesis entitled "Flavour Characterisation and Stabilisation of Fresh, Spray-dried, Freeze-dried and Encapsulated Durian Extract" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the candidate be awarded the relevant degree. Members of the Examination Committee are as follows:

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This thesis submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Master of Science. The members of the Supervisory Committee are as follows:

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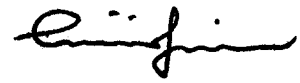

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DECLARATION

I hereby declare that the thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UPM or other institutions.

CHIN SUNG TONG

Date: 24-8-2006

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LIST OF ABBREVIATIONS

%	percent
°C	degree centigrade
°F	degree Fahrenheit
µl	microliter
µm	micrometer
ANOVA	analysis of variance
C	carbon chain
cm	centimeter
DVB/CAR/PDMS	divinylbenzene/carboxen/polydimethylsiloxane
EI	electron ionization
eV	electron voltage
GA	gum arabic
GC	Gas Chromatography
GC/MS	Gas Chromatography / Mass Spectrometry
GC-FID	Gas Chromatography – Flame Ionization Detector
GC-TOFMS	Gas Chromatography – Time Of Flight Mass Spectrometry
i.d.	internal diameter
kg	kilogram
L	liter
m	meter
MD	maltodextrin DE15

MG	blending of 3 part MD with 1 part GA
min	minute
ml	milliliter
mm	millimeter
ND	not detected
PC	principal component
PDMS / DVB	polydimethylsiloxane / divinylbenzene
PDMS	polydimethylsiloxane
ppm	parts per million
RH	relative humidity
rpm	revolution pre minute
RSD	relative standard deviation
s	second
SDE	Simultaneously Distillation Extraction
SPME	Solid Phase Microextraction
Ti	inlet temperature
To	outlet temperature

CHAPTER I

GENERAL INTRODUCTION

Durian (*Durio zibethinus*), which belongs to a member in the *Bombaceae* family is a most favoured and expensive fruit in Southeast Asia countries. Durian species growth originated from the Malay Peninsular and now, over 20 durian varieties can be found in the Malaysian market but only certain varieties are much preferred. Durian pulp with firm, fine texture possesses 2 distinct types of aroma; which is the sulfury onion-like and delicately fruity odour. Studies have been carried out to determine the volatile and non-volatile substances that are responsible for durian flavour perception. A total of 137 durian volatile constituents were reported. Nevertheless, limited information is available regarding the flavour volatile composition that discriminate the preferred durian varieties.

The availability of durian for 4 to 5 months in a year has driven Malaysian government to increase the production of durian. However, the market for durian in Malaysia is mainly for domestic consumption whereas exportation has been constrained due to the difficulty of fruit transportation, and limited shelf life of 2 to 5 days if without refrigeration. Processing of durian into dried powder form is advantageous to overcome these market restrictions. Dehydration or drying process is widely used in preserving fruit and vegetables due to the benefits of reduced costs, added convenience, and excellent product stability against microorganisms and undesired biochemical reaction.

However, dehydration of food products were reported to result in noticeable flavour-losses and increase in off-flavour notes after exposure to high temperature treatment during drying, which subsequently altered the original flavour perception. From the standpoint of quality control and process optimization, understanding of the drying effect on flavour and odour of durian products during processing would be desirable.

Several factors have to be considered during the analysis of volatile compounds in food that include sensitivity of current instrument; complexity of food matrix and stability of flavour compounds during extraction. Solid phase microextraction (SPME) provides advantages such as eliminating the use of solvent, inexpensive, rapid and easy to use, compatibility with a wide range of analytical instruments, and improved detection limits. Meanwhile, fast gas chromatography (fast GC) technique offers the advantage of high-speed chromatography on complex sample without sacrificing data quality whilst Time-of-Flight Mass Spectrometry (TOFMS) with high spectra acquisition rate was found suited for volatile organic compounds detection in a very-fast GC. To date, the conjunction of SPME technique with fast GC and TOFMS system has been demonstrated as a suitable tool for rapid characterization and quality evaluation of some food materials. In fact, calibration or optimization of the utilized conditions is necessary to enhance the sensitivity and accuracy in the routine analysis on volatile profile of durian products in both qualitative and quantitative terms.

Loss of durian flavour volatiles during spray drying could be minimized substantially by implementing the concept of selective diffusion in microencapsulation for volatiles

retention effect. The effect of volatiles encapsulation can be perceived by the incorporation of coating or carrier material with excellent film-forming properties into the feed stock prior to spray drying. Factors including spray drying parameters and feed stock properties are important to determine for improved encapsulating efficiency.

The goals of the present study were

1) to analyze the flavour volatiles of fresh durian pulp from 3 well-known varieties in Malaysia (*D24*, *D2*, *D101*) using headspace SPME coupled to fast GCMS and further distinguish these varieties according to their volatiles composition.

2) to determine the effect of spray drying and freeze drying process on the flavour volatiles from durian pulp using headspace SPME coupled to fast GC-TOFMS.

3) to investigate the influence of the drying conditions and type of coating materials on the stability of durian flavour volatiles during spray dry microencapsulation.